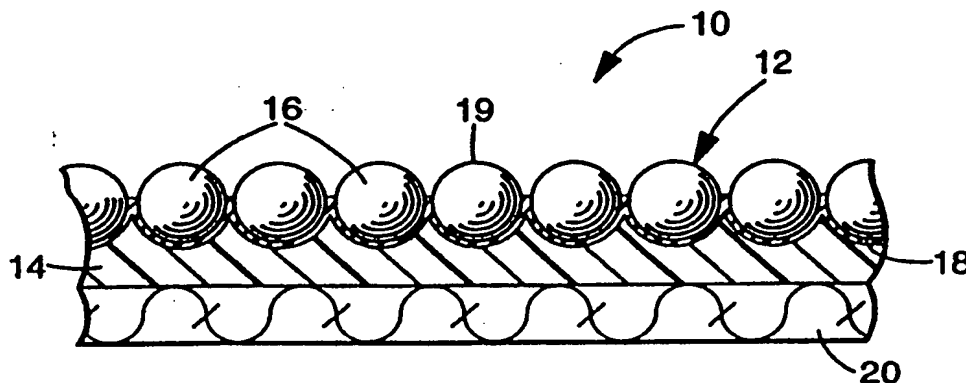




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**(54) Title:** RETROREFLECTIVE ARTICLE HAVING LAUNDERABLY DURABLE BEAD-BOND

**(57) Abstract**

A retroreflective article (10) has retroreflective elements (12) partially embedded in a binder layer (14) that contains a solid polyurethane. The polyurethane includes soft segments, hard segments, silicon moieties, and urethane moieties. The specific chemical identities and relative amounts of the segments and moieties are sufficient to impart desired high elongation and low modulus to the polymer. The inventive retroreflective article is capable of demonstrating extraordinary laundering durability under industrial wash conditions and tumble and tunnel drying.

**RETROREFLECTIVE ARTICLE HAVING LAUNDERABLY DURABLE BEAD-BOND**

This invention relates to retroreflective materials or articles, such as fabric or sheeting that can be attached to garments to enhance nighttime visibility of the wearer. In another aspect, the invention relates to articles comprising retroreflective elements, e.g., transparent microspheres or beads with hemispheric reflectors, partially embedded in a layer of a binder, e.g., polyurethane. In other aspects, this invention relates to polyurethanes, particularly silicon-containing, moisture-cured polyurethanes, useful as such a binder, to methods of making polyurethanes, and to the use of polyurethanes as bead-bond binders to make retroreflective articles which are to be laundered.

In order to improve visibility or safety of pedestrians, joggers, workers on roadways, etc., retroreflective markings have been attached to their clothing to reflect light back in the direction of the incident light beam or source, such as that of automobile headlights, so that the presence of such persons are highlighted or made conspicuously visible to prevent them from being struck by an oncoming vehicle. Such retroreflective articles are described, for example, in U.S. Pat. No. 5,200,262 (Li), International Pat. Appln. published as WO 96/16343, and U.S. Pat. No. 5,474,827 (Crandall et al.). As stated in the latter reference, a retroreflective article typically comprises a layer of optical elements, a polymeric binder layer, and a specular reflective layer. The optical elements usually are transparent microspheres that are partially embedded in the polymeric binder layer (or bead-bond), and the specular reflective layer is disposed beneath the embedded portion of the microspheres.

Other patents describing retroreflective articles include U.S. Pat. Nos. 3,758,192 (Bingham), 4,533,592 (Bingham), 4,576,850 (Martens), 4,725,494 (Belisle et al.), 4,763,985 (Bingham), and 5,378,520 (Nagaoka et al.). The binders for the retroreflective elements are described in several of these patents as certain polyurethanes, e.g., polyurethanes made or used with coupling agent or adhesion promoter, such as isocyanate-functional silane (see said U.S. Pat. Nos. 5,200,262 and 5,474,827 and International Pat. Appln. WO 96/16343). Certain silicon-

The present invention provides, in one aspect, a silicon-containing, solid polyurethane polymer, useful as a polymeric binder for a retroreflective article or material, such as a fabric or sheeting, comprising a monolayer of retroreflective optical elements or lenses (such as transparent or light-transmissible microspheres or beads coated with specular reflective metal to provide them with hemispheric reflectors) partially embedded in (and thus exposed or protruding from) the top or first surface of a binder or "bead-bond" layer comprising the polyurethane polymer. The polymer comprises: a plurality of soft (flexible) segments such as those of (a) a segment comprising polyvalent ester or polyester moieties, e.g.,

5  $(-R^1-C(O)O-)_n$ , where  $R^1$  can be an alkylene, such as pentamethylene, and  $n$  can be 1 to 5 or higher, and/or (b) a segment comprising poly(alkoxy) moieties,  $(-R^2-O-)_m$ , where  $R^2$  can be an alkylene such as tetramethylene, and  $m$  can be 2 to 5 or higher; a plurality of hard (rigid) segments such as those comprising one or more polyvalent carbocyclic groups, e.g., divalent phenylene,

15  $-C_6H_5-$ , or cyclohexylene,  $-C_6H_{10}-$ ; a plurality of silicon moieties,  $\begin{array}{c} | \\ -Si- \\ | \end{array}$ , or siloxy moieties,  $\begin{array}{c} | \\ -OSi- \\ | \end{array}$ ; and a plurality of urethane (or carbamato) moieties,

20  $-N(H)C(O)-$ . The soft segments in a polymer can be the same or different, as is also true of the hard segments. The polymer can be made from a low solvent or essentially solvent-free (or "100% solids") liquid or coatable reaction mixture that can be processed (e.g., coated on a substrate) as such in making the bead-bond of retroreflective articles. The polymer is solidified or crosslinked upon exposure to

25 ambient air or moisture-containing atmosphere and upon standing (aging or curing), and the polymer thus may also contain a very small amount of a plurality of urea (or ureylene) moieties,  $-N(H)-C(O)-N(H)-$ , and/or a small amount of a plurality

30 of hydrolyzed siloxy moieties,  $\begin{array}{c} | \\ -Si(OH)- \\ | \end{array}$ .

The specific chemical identities and relative amounts of said soft and hard segments and silicon and urethane moieties are sufficient to impart desired high elongation and low modulus to the polymer, so that a test specimen of the polymer,

groups, with urethane moieties linking the hard and soft segments; (b) chain-  
extenders, such as alkoxyated bisphenol A diol and low molecular weight polyol;  
and (c) isocyanatosilane or mercaptosilane; and (2) exposing the resulting  
embedded layer to ambient air (viz., moisture-containing atmosphere) and letting it  
5 stand (or age) over a sufficient period of time (e.g., 2 to 6 weeks) to form from the  
mixture a binder layer comprising silicon-containing crosslinked polyurethane. The  
specific chemical identities and relative amounts of the segments and the silicon and  
urethane moieties in the polyurethane are sufficient to impart desired high  
elongation (e.g., greater than 500%) and low modulus (e.g., Young's modulus and  
10 100% modulus of less than 10 MPa, preferably less than 2 MPa) to the  
polyurethane, thereby rendering it laundry durable, which is manifested by the  
substantial retroreflectivity of the article after many repeated launderings or wash-  
drying cycles, e.g., 5 to 15 or even in some cases up to 40 or more.

An example of the silicon-terminated polyurethane of this invention is that  
15 formed by an essentially solvent-free method of mixing (1) an isocyanate-terminated  
urethane prepolymer made by condensation polymerization of a polyol, such as a  
poly(caprolactone)-poly(tetramethylene oxide)-poly(caprolactone) block copolymer  
diol, and a carbocyclic polyisocyanate, such as methylene bis(4-  
cyclohexylisocyanate), with (2) a mixture of an ethoxylated bisphenol A diol, a low  
20 molecular weight polyol such as trimethylolpropane or ethoxylated  
trimethylpropane (MW 267), and an isocyanatosilane, such as triethoxyiso-  
cyanatosilane, or a mercaptosilane, and allowing the resulting reaction mixture, after  
shaping or coating the same in ambient air or in the presence of moisture-containing  
atmosphere, to cure and to form a silicon-containing, chain-extended, crosslinked,  
25 solid polyurethane useful as a binder or "bead-bond" for retroreflective elements.

The silicon-containing polyurethane of this invention also can be made by a  
"one-shot" (or single step) technique by directly mixing the isocyanato- or  
mercaptosilane with the precursors of the hard and soft segments and urethane  
linking groups, namely, polyol, polyisocyanate, and chain-extenders. The ensuing  
30 reaction is relatively fast upon mixing and is carried out in the presence of catalyst  
to promote urethane bond-forming.

or a first surface of a binder layer or "bead-bond" 14. Each of the retroreflective elements 12 includes optical element in the form of a transparent microsphere or bead 16 and a specularly reflective layer 18. Light that strikes the front or exposed top 19 of the retroreflective article passes through the microspheres 16 and is reflected by reflective layer 18 to again re-enter the microspheres where the light's direction is again altered to return a substantial quantity of the incident light towards the light source. A layer of fabric 20, such as polyester, is bonded to the opposite side or second surface of the binder layer 14 to increase the structural integrity of the article 10. The article 10 may be applied or affixed, e.g., sewn, as a trim to a substrate (not shown), such as a garment, e.g., a vest.

Retroreflective article 10 can be made by first forming article 30 shown in FIG. 2. In forming article 30, a multitude of the retroreflective elements 12 are partially embedded in carrier web 32 which comprises a heat-softenable polymer layer 34 and paper sheet 36. Embedding the retroreflective elements can be accomplished by cascading transparent microspheres 16 onto a carrier web 32 in a desired temporary arrangement. Microspheres 16 preferably are packed as closely as possible on the carrier web 32, and may be so arranged by any convenient process, such as printing, screening, cascading, or with a hot can roll. Examples of useful polymer layers 34 for carrier web 32 include polyvinyl chloride, polyolefins, such as polyethylene, polypropylene, and polybutylene, and polyesters. Methods of applying microspheres to such a carrier web are described, for example, in U.S. Pat. Nos. 4,763,985 (Bingham), 5,128,804 (Lightle *et al.*), and 5,200,262 (Li), which descriptions are incorporated herein by reference.

Polymer layer 34 retains microspheres 16 in the desired arrangement. Depending in part on the characteristics of the carrier web 32 and microspheres 16, it may be desirable to condition carrier web 32 and/or microspheres 16 by applying selected release agents or adhesion promoters to achieve desired carrier release properties.

A reflective layer 18 is applied to carrier web 32 on the surface from which the microspheres protrude. The size of the retroreflective elements 12, as indicated by the portion of the microspheres covered with the reflective layer 18, may be controlled in

illustration, the article of clothing of the invention can be in a variety of forms. As the term is used herein, "article of clothing" or "garment" means a launderable item of wearing apparel sized and configured to be worn or carried by a person. Other examples of articles of clothing that may display retroreflective articles of the invention  
5 include shirts, sweaters, jackets, coats, pants, shoes, socks, gloves, belts, hats, suits, one-piece body garments, bags, and backpacks.

Except for the particular binder layer 14 mentioned in the above description of the drawing, the retroreflective articles are known -- see, for example, said International Pat. Appln. WO 96/16343.

10 The binder layer of the retroreflective articles of this invention can be derived from an isocyanate-terminated polyurethane prepolymer that is a reaction product of (i) a polyol which provides requisite soft segments, such as a polyester-polyalkoxy-polyester ABA block copolymer polyol, preferably one having a number average molecular weight of at least 2,000, and (ii) a carbocyclic polyisocyanate, such an  
15 aromatic or cycloaliphatic diisocyanate which provides requisite hard segments. The prepolymer contains urethane groups,  $-N(H)C(O)-$ , which form when the hydroxyl groups of the polyol react with some of the isocyanato groups of the polyisocyanate. The isocyanate-functional polyurethane prepolymer is then mixed with aromatic or cycloaliphatic polyol chain-extender which provides further hard segments, a low  
20 molecular weight triol chain-extender, and mono- or poly(alkoxy) isocyanato-silane or mercapto-silane. A catalyst also may be added to the resulting reaction mixture to promote the cure of the resulting reaction mixture to form a cross-linked, silicon-containing, polyurethane polymer.

In order to have sufficient time to process the reaction mixture that forms the  
25 polyurethane bead-bond, a delay catalyst can be incorporated into the reaction mixture. Such catalyst will cause the viscosity of the reaction mixture, after it is coated as a bead-bond or binder layer, to slowly rise over period of time, e.g. up to 20 minutes, to permit continuous producing or processing of a uniform, solvent-free (or 100% solids) polyurethane coating and then quickly cause the layer to rise in viscosity and effect cure  
30 at elevated temperature of the reaction mixture. Delay catalyst suitable for this purpose are zinc and bismuth carboxylates, as described in more detail hereinafter.

poly(tetramethylene glycol), Acclaim™ 8200 poly(propylene oxide), and Tone™ 2241 poly(caprolactone).

The polyisocyanate used to make the polymer of this invention is preferably an aromatic polyisocyanate. Examples of aromatic polyisocyanates include toluene diisocyanate (TDI), methylene-bis(4-phenyl) isocyanate (also referred to as diphenyl methane diisocyanate or MDI), xylene diisocyanate, and polyphenylene polymethylene isocyanate (PMDI). Commercially available polyisocyanates which can be used include Mondur™ ML isomeric mixture of diphenylmethane diisocyanates, Desmodur™ W dicyclohexylmethane-4,4'-diisocyanate, Desmodur™ CB-75N aromatic polyisocyanate adduct based on toluene diisocyanate and dissolved in ethyl acetate, and Hylene™ PPDI p-phenylene diisocyanate. Other polyisocyanates which can be used as hard segment precursors are those described in said U.S. Pat. No. 4,576,850.

Alternatively, instead of making an isocyanate prepolymer and then mixing it with the chain-extender and silane materials, commercially-available prepolymers can be mixed with these materials, such as Adiprene™ 150 and Versathane™ SME 90A prepolymers, derived from 1000 MW poly(tetramethylene glycol) and para-phenylene or di-phenylene diisocyanate.

Useful chain extenders (or crosslinkers) that can be used to make the polymer of this invention include low molecular weight diols (e.g., diols with molecular weights of about 90 to 600) and triols, such as 1,6-cyclohexane dimethanol, 1,6-hexane diol, 2-methyl-1,3-propane diol, glycerine, and trimethylolpropane. High molecular weight products can be used as chain-extendors to make the polyurethane polymers of this invention, such as Dianol™ 265, Dianol™ 240/1, and SynFac™ 8009 ethoxylated bisphenol A products, Stepanol PS1752 and Stepanol PS20-200A diethylene glycol-phthalic anhydride-based polyester polyols, Poly THF™ poly(tetrahydrofuran), Voranol™ 234-630 triol, Rucoflex™ F-2300 polyester triol, and Tone™ 0305 poly(caprolactone) triol. The ethoxylated bisphenol A diol used to chain-extend the prepolymer is preferably said Dianol™ 265 diol, which has a molecular weight of 510 and a hydroxyl number of 220 mg KOH/g. Mixtures of chain-extendors can be used. Preferably, to obtain the desired high elongation in the polyurethane product used as a bead-bond, the chain-extender has a linear, saturated aliphatic chain containing one or

In addition to the above components, the reaction mixture used to prepare the polyurethane of this invention contains, as an adhesion promoter, hydrolyzable silanes that are isocyanato-functional or mercapto-functional, such as the products commercially available from Witco Chem. Co. as A-1310 isocyanatotriethoxysilane and  
5 A-189 mercaptopropyltrimethoxysilane. (The isocyanate functionality of the isocyanato-silane is not included in the calculation of the NCO/OH ratio of the polyurethane reaction mixture.) The amount of silane to be used is an amount sufficient to increase the adhesion of the polyurethane. Generally the amount will be 0.5 to 10 wt %, preferably 1 to 5 wt %, of the polymer.

10 Additionally, the silicon-terminated polyurethane binder layer may contain colorants (for example, pigments, dyes, metal flakes), fillers, stabilizers (for example, thermal stabilizers and antioxidants, such as hindered phenols, and light stabilizers, such as hindered amines or ultraviolet stabilizers), flame retardants, flow modifiers (for example, surfactants, and plasticizers). Care should be taken when selecting such  
15 additives because some may detrimentally affect laundering durability. Preferred colorants for articles having aluminum retroreflective layers include black dyes such as metal-azo dyes.

The binder layer typically is a continuous, fluid-impermeable, polymeric, sheet-like layer which has a thickness of about 1 to 250 microns. Preferably, the thickness is  
20 about 50 to 150 microns. Thicknesses less than 50 microns may be too thin to adhere to both the substrate and the optical elements, and thicknesses greater than 150 microns may unnecessarily stiffen the retroreflective sheeting or fabric and add to its cost.

As indicated above, retroreflective optical elements are supported by the binder layer to alter the direction of light. The optical elements can be microspheres that  
25 preferably are substantially spherical in shape in order to provide the most uniform and efficient retroreflection. The microspheres preferably also are substantially transparent so as to minimize absorption of light so that a large percentage of incident light is retroreflected. The term "transparent" is used herein to mean capable of substantially transmitting light. The microspheres often are substantially colorless but may be tinted  
30 or colored in some other fashion. The microspheres may be made from glass, a non-vitreous ceramic composition, or a synthetic resin. In general, glass microspheres are



Among the many compounds that may be used in providing transparent materials within the desired refractive index range are high index materials such as CdS and the like, and low index materials such as  $\text{Al}_2\text{O}_3$ , and the like.

5

#### EXAMPLES

Advantages and objects of this invention are further illustrated in the Examples set forth hereafter. It is to be understood, however, that while the examples serve this purpose, the particular ingredients and amounts used and other conditions recited in the Examples are not to be construed in a manner that would unduly limit the scope of this invention. The Examples selected for disclosure in here are merely illustrative of how to make various embodiments of the invention and how the embodiments generally perform.

10

The following test methods were used in the Examples.

#### 15 Industrial Laundering Procedure

Launderability of various retroreflection articles of this invention, prepared as described below, was evaluated in each Example by washing and drying a piece of fabric to which the retroreflective article was applied. The combined sequence of washing and drying is referred to as a laundering cycle. The samples were washed using a Milnor System 7 Washing Machine Model 30015M4G from Pellerin Milnor Corp. in accordance with Program No. 7 for heavily soiled, colored fabrics. Launderability was evaluated by washing and drying a piece of 100% cotton towel fabric to which the retroreflective article was sewn. The cleaning agents used were 90 ml of Lever Tech Ultra™, a detergent containing, by weight, approximately 10% potassium hydroxide, 25% potassium citrate, and 2% ethoxylated lauryl alcohol, and 120 ml of Lever Tech Booster™ (a pH builder containing 20% sodium hydroxide). The washer was loaded with enough pieces (approximately 80) of fabric (about 45 cm by 75 cm) to make a 28 pound (12.7 kg) load including from one to four pieces of fabric having several (typically about 5) retroreflective articles of the invention (about 5 by 15 cm in size) secured thereto.

30

### Retroreflective Brightness Test

The coefficient of retroreflection was measured in accordance with standardized test ASTM E 810-93b, and is expressed in candelas per lux per square meter, (cd/lx • m<sup>2</sup>). The entrance angle used in ASTM E 810-93b was -4 degrees and the  
5 observation angle was 0.2 degrees. (Said entrance angle of -4 degrees gives results which are not significantly different than the entrance angle of +5 degrees used in said British Standard BS EN 471:1944).

### Tensile Elongation and Modulus Tests

10 Tensile, elongation, and modulus tests of the polyurethanes described in the Examples were performed on a MTS (Materials Testing Systems) machine or an Instron Model 5565 machine. The polyurethane films were cut into 0.5 inch by 2-inch (1.3 cm x 5.1 cm) strips and put into the grips of the machine set at a 1-inch (2.5 cm) gauge length. Tests were performed with a cross-head speed of 10 or 20  
15 inches/minute (25 or 50 cm/min).

### Examples 1-13

For each of the Examples, glass microspheres having an average diameter of about 40 to 90 micrometers were partially embedded in a carrier web. The carrier web  
20 contained juxtaposed paper and polyethylene layers, and the microspheres were embedded in the polyethylene layer. A specularly-reflective aluminum layer was vapor deposited over the protruding portions of the glass microspheres to form a monolayer of retroreflective elements. This embedded carrier web was used as the base for applying the bead bond formulation prepared as follows:

25 In Example 1, an amount of 19.4 grams (0.022 equivalents) of Terathane CL polyether glycol was heated in an oven to 50°C and then 5.5 grams (0.044 equivalents) Mondur ML was added and then stirred. One drop (~0.03 grams) dibuytindilaurate (DBTDL) was added to the resulting mixture and stirred. The resulting reaction  
30 mixture was allowed to react for 30 minutes while maintaining its temperature at 50°C, with occasional stirring. A mixture of 2.5 grams cyclohexanone, 2.5 grams methyl ethyl ketone, and 0.9 gram of triethoxysilane was then added to the resulting

Table 2

	EXAMPLES												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Polymer Binder Formulation, g													
Terathane CL polyol	19.4	19.4	0	0	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4
Terathane 2000 polyol	0	0	22.0	0	0	0	0	0	0	0	0	0	0
Tone 2241 polyol	0	0	0	22.0	0	0	0	0	0	0	0	0	0
Acclaim 8200 polyol	0	0	0	0	0	0	0	0	0	0	0	4.6	0
Mondur ML polyisocyanate	5.5	5.1	5.1	5.1	5.1	5.1	5.0	0	5.5	6.88	5.1	5.1	5.1
Desmodur W polyisocyanate	0	0	0	0	0	0	0	5.28	0	0	0	0	0
DBTDL catalyst	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.03
Cyclohexanone	2.5	2.5	2.5	2.5	2.5	2.5	2.5	0	2.5	2.5	2.5	0	2.5
Methyl ethyl ketone <sup>a</sup>	2.5	2.5	2.5	2.5	2.5	5.5	2.5	0	2.5	2.5	2.5	0	2.5
Methyl ethyl ketone <sup>b</sup>	5.0	5.0	5.0	5.0	5.0	0	5.0	0	5.0	5.0	3.0	3.0	5.0
Irganox 1010 stabilizer	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0	0.2	0.2	0.2	0.28	0.2
Butanediol	0	0	0	0	0.54	0	0	0	0	0	0	0	0
Syn Fac 8009 polyol	0	2.95	2.95	2.95	0	2.95	3.3	3.13	0	0	2.95	2.95	0
Voranol 234-630 polyol	0	0.89	0.89	0.89	0.89	0.89	0.89	0	0	0	0.89	0.89	0.89
Rucoflex F-2300 polyol	0	0	0	0	0	0	0	1.82	0	0	0	0	0
Dianol 265 polyol	2.75	0	0	0	0	0	0	0	2.32	5.34	0	0	0
Trimethylolpropane	0.45	0	0	0	0	0	0	0	0.54	0.45	0	0	0
Polymer Binder Formulation, g (continued)													
Stepanol PS 1752 polyol	0	0	0	0	0	0	0	0	0	0	0	0	3.89
A-189 Mercaptosilane	0	1.0	0	0	0	0	0	0	0	0	0	0	0

The data of Table 2 show that various formulations of the polyurethane bead-bond of this invention exhibited laundering durability. Note that all the samples of the Examples had substantial retention of retroreflectivity. By comparison, a binder formulation that did not contain any silane resulted in a retroreflective article which had a retroreflectivity of less than 100 cd/lx • m<sup>2</sup> after only one laundering cycle. The samples of all the Examples also had low modulus (<10 MPa) and high elongation at break (>500%), which properties account, at least in part, for the bead-bonds of those samples withstanding the harsh or severe washing and drying laundering conditions stresses incurred during washing and drying. The data also show that amounts of the polyisocyanate and chain-extender, used to obtain desired high laundering durability in a particular type of drying (tumble or tunnel), can be varied (cf Examples 7 and 11). Such amounts can be readily found empirically. Too high amounts of chain extender and polyisocyanate has been found to result in a polyurethane with an elongation of less than 500% and a modulus of greater than 10 MPa, with consequent poor laundering durability, e.g., a retroreflectivity of less than 100 cd/lx • m<sup>2</sup> after one laundering cycle.

#### Example 14

Table 3 sets forth the formulations of two mixtures, M-1 and M-2, used to make a polyurethane bead-bond of this invention.

Table 3

<u>Mixture M-1</u>	<u>Mixture M-2</u>
Terathane CL polyol, 16.227 Kg	Mondur ML polyisocyanate, 9.487 Kg
Voranol 2334-630 polyether triol, 0.74 Kg	A-1310 silane, 1.860 Kg
SynFac 8009 polyol, 2.46 Kg	
DBTDL catalyst, 6.1 g	

Mixture M-1 was heated in a tank to 160°F (71°C) and Mixture M-2 was held in a tank at ambient temperature. Mixture M-1 was pumped at 71.5 g/min into a pin mixer and Mixture M-2 was pumped into the pin mixer at 19.51 g/min. The

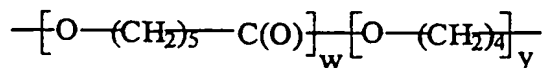
Table 3

<u>Mixture M-3</u>	<u>Mixture M-4</u>
Terathane CL polyol, 15.99 Kg	Mondur ML polyisocyanate, 9.487 Kg
Voranol 2334-630 triol, 0.73 Kg	A-1310 silane, 1.860 Kg
SynFac 8009 polyol, 2.43 Kg	
Bicat 8 catalyst*	
Bicat Z catalyst*	
* dissolved in 66.93 g of Santicizer 141 when added	

The resulting retroreflective article had an initial retroreflectivity of 519 cd/lx • m<sup>2</sup> and was laundered, after aging 2 weeks in ambient atmosphere similar to that of Example 14. The retroreflectivity of the article after 25 industrial laundering cycles using a Maytag dryer was 250 cd/lx • m<sup>2</sup>, and after 2 laundering cycles using tunnel drying conditions, retroreflectivity of the article still exceeded 100 cd/lx • m<sup>2</sup>.

Various modifications and alterations of this invention will be apparent to one skilled in the art from the description herein before without departing from the scope and spirit of this invention.

8. A retroreflective article comprising a layer of retroreflective glass microspheres partially embedded in a binder layer comprising crosslinked, silicon-containing polyurethane polymer comprising a plurality of soft segments of



where w is 4 and y is 7, a plurality of hard segments comprising diphenylene, a

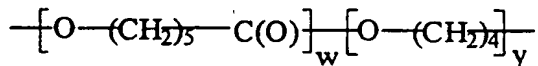
plurality of  $\text{---Si---O---}$  moieties, and a plurality of urethane moieties, the

polymer having an elongation at break of at least 750 and a Young's modulus of less than 10 MPa, the article having a coefficient of retroreflectivity of at least 100 cd/lx • m<sup>2</sup>.

9. A polyurethane comprising a plurality of soft segments, a plurality of hard segments, a plurality of silicon moieties, and a plurality of urethane moieties, the specific chemical identities and relative amounts and ratios of the segments being sufficient to impart to the polyurethane an elongation at break of at least 500 percent and a Young's modulus of less than 10 MPa.

10. The polyurethane of claim 9, wherein the soft segments are polyvalent polyester moieties and/or poly(alkoxy) moieties, and the hard segments comprise carbocyclic groups.

11. The polyurethane of claim 9, wherein the soft segments are



where w is 4 and y is 7, and the hard segments comprise diphenylene.

12. A method of making a retroreflective article comprising (1) partially embedding a layer of retroreflective elements in a surface of binder layer comprising a mixture of (a) an isocyanate-terminated prepolymer of a polyol comprising a plurality of soft segments and a plurality of hard segments, urethane moieties linking

being sufficient to impart desired high elongation and low modulus to the polyurethane and launderably durable retroreflectivity to the polyurethane.

17. The method of claim 6 wherein the catalyst is zinc carboxylate,  
5 bismuth carboxylate, or mixtures of the carboxylates.

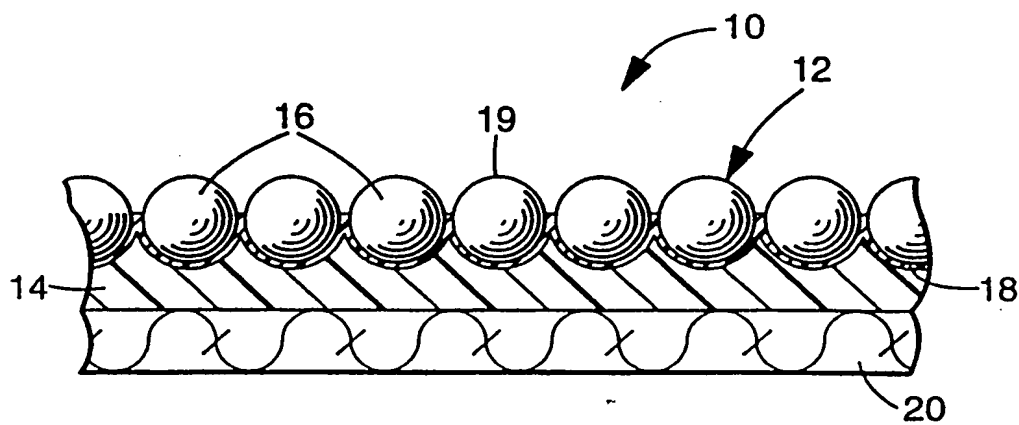
18. A method of making a polyurethane, which method comprises  
mixing together isocyanate-terminated urethane prepolymer of a polyol comprising  
a plurality of soft segments of polyvalent polyester moieties and polyvalent  
10 polyalkoxy moieties, a plurality of hard segments of polyvalent carbocyclic groups,  
and a plurality of urethane moieties, ethoxylated bisphenol A diol, low molecular  
weight polyol, and mercaptosilane or isocyanatosilane, and exposing the resulting  
mixture to ambient air to form from the mixture a polyurethane, the specific  
chemical identities and relative amounts and ratios of the segments being sufficient  
15 to impart desired high elongation and low modulus to the polyurethane.

19. A method of making a polyurethane, which method comprises  
mixing together carbocyclic polyisocyanate, polyol comprising a plurality of soft  
segments of polyvalent polyester moieties and polyvalent polyalkoxy moieties,  
20 ethoxylated bisphenol A diol, low molecular weight polyol, and mercaptosilane or  
isocyanatosilane, and exposing the resulting mixture to ambient air to form from the  
mixture a polyurethane, the specific chemical identities and relative amounts of the  
segments being sufficient to impart desired to impart to the polyurethane an  
elongation at break of at least 500 and a modulus of less than 10 MPa.

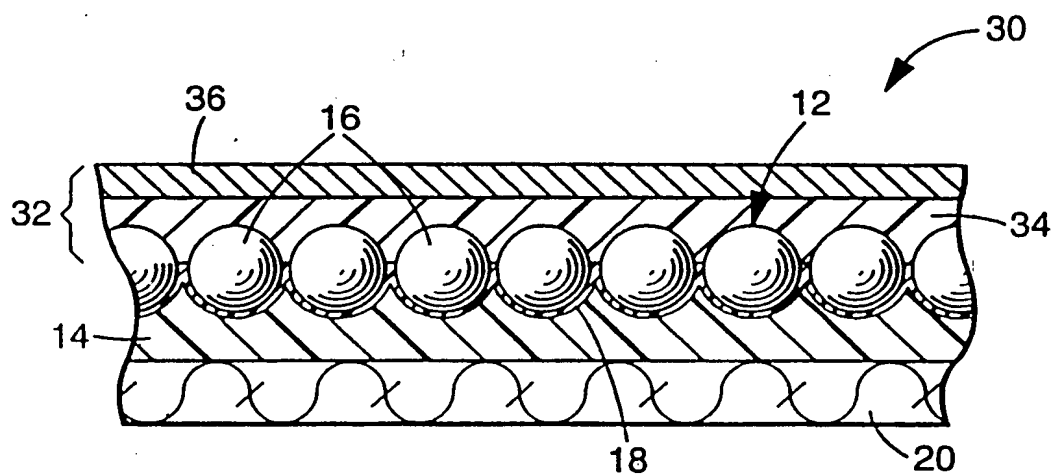
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20. The method of claim 19, wherein the polyol is poly(caprolactone) -  
poly (tetramethylene oxide) block copolymer.

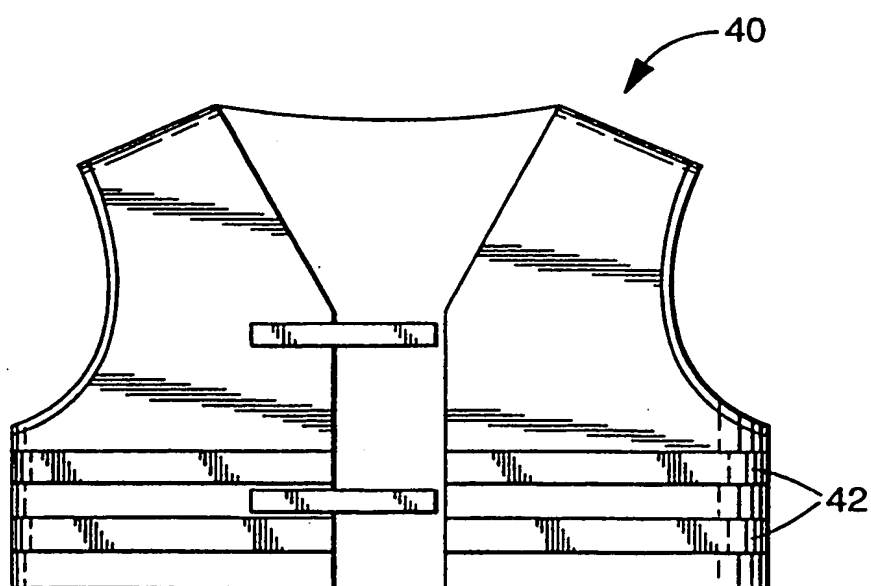
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**Fig. 1**



**Fig. 2**



**Fig. 3**



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/23040

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G02B5/128 C08G18/71 C08G18/61

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G02B C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 200 262 A (LI WU-SHYONG) 6 April 1993 cited in the application see claims 1-21 see column 4, line 64 - column 5, line 44 ---	1-20
X	WO 96 16343 A (MINNESOTA MINING & MFG) 30 May 1996 cited in the application see claims 1,10 see page 6, line 25 - page 7, line 8 see page 7, line 27 - line 30 see page 17; table 1 --- -/--	1-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

6 March 1998

Date of mailing of the international search report

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Information on patent family members

International Application No

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